PATENT SPECIFICATION

(11) 1 594 223

(21) Application No. 2533/77 (22) Filed 21 Jan. 1977

(23) Complete Specification Filed 19 Jan. 1978

(44) Complete Specification Published 30 Jul. 1981

(51) INT. CL.[3] G01N 27/56

(52) Index at Acceptance
G1N 19LM 25A2 25C4B2 25C4B 25C4D 25D6 BPS

1 594 223

(19)

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(54) THE DETERMINATION OF HYDROGEN

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute, of Kingsgate House, 66 - 74 Victoria Street, London, S.W.1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to the determination of small quantities of hydrogen normally in the presence of other substances including other gases, and in particular to the determination of hydrogen impurities in molten metals or alloys.

The presence of hydrogen in molten metals poses a serious problem often causing lowering of the tensile strength of cast products. For instance, hydrogen present in molten aluminium gives rise to the formation of cracks and voids as the metal solidifies seriously diminishing the resultant strength properties. In consequence, therefore, it is highly desirable to determine the hydrogen content of the molten metal before casting, although techniques hitherto available, such as that in which hydrogen is removed under vacuum from the heated metal and recovered by condensation at liquid nitrogen temperatures, are far too cumbersome to be satisfactory for this purpose. A galvanic technique has now been devised by means of which the hydrogen content of molten metal such as aluminium may be simply and quickly determined.

In accordance with the present invention a process for the determination of the hydrogen concentration present in a substance comprises monitoring the e.m.f. generated between the substance and a reference material which are separated from one another by a solid electrolyte comprising a metal hydride, in which the electrolyte is sealed from the atmosphere prior to use, and the seal is removed on introduction of the electrolyte to the substance.

The invention also includes apparatus for the determination of the hydrogen concentration present in a substance, comprising a probe in the form of a tube of insulating ceramic material, closed at one end by a pellet of metal hydride solid electrolyte, the tube containing reference material, and in which the solid electrolyte is sealed from the atmosphere prior to use.

The probe is typically provided with means for electrically connecting the substance and the reference side of the solid electrolyte with a suitable e.m.f. measuring device e.g. a high impedance voltmeter, for instance, means in the form of electrically conducting metal electrodes.

The apparatus and method of the present invention are particularly useful for the determination of hydrogen present in molten metals or alloys; though it will be appreciated that the invention may be applied to the determination of hydrogen in other environments, for instance hydrogen present in reducing gas mixtures such as those which are encountered in the petrochemical industry.

The hydride solid electrolyte of the present invention typically comprises an ionic hydride such as, for instance an alkali or alkaline earth metal hydride, e.g., LiH, NaH, KH, RbH, CsH, CaH_2, SrH_2, BaH_2, BeH_2, MgH_2. To withstand the extremes of temperature of molten metals the hydride is preferably of high melting point e.g. melting point greater than about 500°C, and preferred hydrides are lithium hydride, sodium hydride, barium hydride and especially calcium hydride.

The reference material used in the present invention typically exhibits a constant hydrogen activity under the conditions at which determination is carried out e.g. at the elevated temperatures of molten metals.

Thus the reference material may comprise hydrogen gas or any other suitable hydrogen containing material, though leaks of hydrogen gas may cause inaccuracies in the results obtained. Preferably the reference material is solid and more preferably consists of a metal/metal hydride mixture. Such metal/metal hydride reference materials may comprise any suitable metal including all those metals discussed previously in the context of metal hydride solid electrolytes. In particular the reference material may consist of a metal/metal hydride mixture having the same metal component as the solid electrolyte, especially a calcium/calcium hydride mixture.

It will be appreciated that metal hydrides are subject to atmospheric attack and undergo rapid deterioration on exposure to air. Thus the solid electrolyte of probes in the present invention is sealed from the atmosphere prior to use. In one embodiment, the external surface of the solid electrolyte is sealed from the atmosphere by a layer of metal e.g. aluminium, foil, which is preferably held in place by a suitable adhesive such as an impact adhesive e.g. "Permabond" (Permabond is a Registered Trade Mark). Generally also the internal surface of the solid electrolyte is sealed from the atmosphere, for instance, the other end of the tubular probe is also closed.

In one arrangement an internal electrode passes through a seal in one end of the tubular probe to make electrical contact, either by direct physical contact or through an electrically conducting reference material, with the internal surface of the solid electrolyte at the other end of the tubular probe. Generally there is also an external electrode which contacts the substance when the probe is in use. Such internal and external electrodes are conveniently constructed of suitable corrosion resistant electrically conducting material such as stainless steel or silver steel. The e.m.f. generated between these two electrodes is monitored, preferably using a high impedance voltmeter.

The probe assembly of the present invention may conveniently be provided with a suitable handle or other means to permit manipulation, for instance for introduction of the probe to the molten metal bath. Such a handle is generally provided with insulation to protect the user against the extremes of temperature and also may incorporate electrically conducting members by which the external and internal electrodes may be electrically connected to the voltmeter.

In use the external seal over the solid electrolyte is removed on introduction of the sealed probe to molten metal. For example, at the temperature of molten aluminium the aluminium foil coating melts and the adhesive layer burns off exposing the solid electrolyte to the molten aluminium bath. Generally the probe is discarded after use.

The method and apparatus of the present invention provide a simple and quick means for determining hydrogen particularly advantageous for determining hydrogen in the presence of molten metals or alloys.

The process and apparatus of the invention are further illustrated in the following specific description and Example which refers to the accompanying diagrams in which:-

Figure 1 shows a side view of an axial section through a hydrogen probe according to the present invention;

Figure 2 shows a similar view in diminished scale of the probe of Figure 1 attached to a handle and connected to an operational circuit;

Figure 3 shows a graph of probe e.m.f. against dissolved hydrogen concentration for a molten aluminium bath at 725°C, the hydrogen concentration being determined by two independent quantitative techniques, and compared with a theoretically calculated curve;

Figure 4 shows theoretically calculated curves for hydrogen probe e.m.f. against dissolved hydrogen concentration, in a molten aluminium bath at various temperatures.

The hydrogen probe of Figure 1 is constructed as follows:

One end of an α-alumina tube 1 (length 8 cm, external diameter 4 mm, internal diameter 2 mm) is ground flat, perpendicular to its long axis and a disc of aluminium foil 2 (0.1 mm thick) is glued over this end using "Permabond" contact adhesive 3. The tube 1 is then transferred to an argon filled glove compartment in which the probe is further assembled.

Calcium hydride (min purity 99.5%) is ground to a fine powder and rammed by hand into the end of the tube 1 with a close fitting steel rod to form a cylindrical calcium hydride electrolyte pellet about 5 mm long abutting the aluminium foil disc 2. Calcium granules are then filed to produce finely powdered metallic calcium which is mixed approximately 1:1 with calcium hydride powder to provide a powdered calcium/calcium hydride reference material. The relative proportions of calcium and calcium hydride in the reference may, however, be varied widely, as any mixture of calcium and calcium hydride gives a known partial pressure for a given temperature. This powdered reference is then similarly packed into the tube on top of the electrolyte to form a reference layer 5 of depth about 10 mm which is finally rammed home with a silver steel rod 6 (length 8 cm, diameter 2mm) the

end of which has been ground to a point. The probe is made airtight by sealing its top end with "Autostic" cement 7 and then removed from the glove box and stored under normal atmospheric conditions.

Figure 2 shows the probe 10 of Figure 1 in use in conjunction with a handling device comprising a central steel rod 11 to which, at its lower end, is attached, by a screw fitting, the central silver steel internal electrode 6 of the probe 10. Surrounding the central rod 11 and separating it from an outer steel tube 12 is an insulating silica tube 13. The outer tube 12 has a silver steel rod 14 (length 20 cm, diameter 6 mm) welded to its lower end to provide an external electrode. Also there is a layer of insulating felt 15 taped around the outside of the tube 12 towards its other end to provide a handle to protect the user against the extreme temperatures of the molten metal bath 16 and to avoid interference with the generated e.m.f. The upper ends of the rod 11 and tube 12 are connected to a high impedance voltmeter 19 usually by a coaxial cable, shown diagrammatically as wires 17 and 18 in Figure 2, the internal electrode 6 of the probe 10 normally connected, by way of the central rod 11, to the centre, "high" lead of the cable.

In use the probe 1 and external electrode 14 are dipped into the molten metal e.g. aluminium, bath to a depth not exceeding the length of the α-alumina tube 1; though if the probe is provided with a suitable ceramic insulator (not shown) there is no such limitation upon the depth to which the probe may be immersed. At the elevated temperatures of the molten bath 16 the "Permabond" adhesive 3 immediately burns off and the aluminium foil 2 falls off or melts away exposing the calcium hydride electrolyte 4 to the molten bath 16. After a few minutes the e.m.f. registered by the voltmeter 19 reaches a steady reading, as the hydrogen partial pressure within the probe comes to equilibrium. The hydrogen concentration in the molten bath 16 may be determined from the e.m.f. registered by reference to standard curves, see Figure 4, making suitable adjustment in the case of alloys and other mixtures.

After the determination the probe 10 and external electrode 14 assembly are removed from the molten bath, and the probe 10 is unscrewed from the central rod 11 and discarded, and a fresh probe 10 is connected for the next determination.

Generally the equilibrium or response time is a function of the size of the probe 10, and ideally the electrolyte 4 is a thin, dense pellet and only a small amount of reference material 5 is used. The above design, however, is suitable for construction with relatively unsophisticated laboratory facilities and gives reliable results.

Example

The probe of Figure 1 is used as described above to measure the e.m.f. generated by a molten (725°C) aluminium bath containing hydrogen at various points in time whilst the hydrogen content is varying. Corresponding bath samples are analysed for hydrogen content by two independent tests, the Hycon test and a sub fusion test. The Hycon test consists of heating a sample of molten metal in a crucible evacuating the atmosphere and observing the metal surface and noting the pressure at which bubbles of gas appear, this being related to the hydrogen content of the metal. The subfusion test employed consists of heating the aluminium sample at a temperature just below the melting point, removing gas from the sample by means of a diffusion pump, and storing it in the analytical system at low pressure for determination by physical methods. The results obtained are given as curves A and B respectively in Figure 3.

Figure 3 is a graph showing curves of voltage (m.v.) generated between the probe 10 and external electrode 14 against the volume of hydrogen (ml at STP per 100 g of molten aluminium) and includes for comparison a theoretically calculated curve C. The lower limit of the Hycon test is 0.15 ml H_2/100 g Al and of the subfusion technique 0.04 ml H_2/100 g Al, and by subtracting these values from the experimental values the experimental data come into line with the theoretically calculated curve C, clearly showing the reproducibility of the technique of the present invention.

Figure 4 shows a series of experimentally calculated curves 1 to 4 for e.m.f. generated against hydrogen content at various temperatures. The calculated curves may be used as a comparison to determine hydrogen content from e.m.f. data obtained with unknown bath samples.

WHAT WE CLAIM IS:-

1. A method for the determination of the hydrogen concentration present in a substance comprising monitoring the e.m.f. generated between the substance and a reference material which are separated from one another by a solid electrolyte comprising a metal hydride, in which the electrolyte is sealed from the atmosphere prior to use, and the seal is removed on introduction of the electrolyte to the substance.

2. A method according to Claim 1, in which the solid electrolyte comprises lithium, sodium, barium or calcium hydride.

3. A method according to Claim 2, for determination of the hydrogen concentration present in a molten metal or alloy.

4. A method according to any of the preceding Claims, in which the reference material consists of a calcium/calcium hyd-

ride mixture.

5. A method according to any of the preceding Claims substantially as hereinbefore described and illustrated with particular reference to the example and accompanying diagrams, Figures 1, 2, 3 and 4.

6. Apparatus for the determination of the hydrogen concentration present in a substance comprising a probe in the form of a tube of an insulating ceramic material, closed at one end by a pellet of metal hydride solid electrolyte, the tube containing reference material, and which the solid electrolyte is sealed from the atmosphere prior to use.

7. Apparatus according to Claim 6, comprising means for electrically connecting the substance and the reference side of the solid electrolyte with a suitable e.m.f. measuring device.

8. Apparatus according to Claim 6 or 7, in which the solid electrolyte comprises an alkali or alkaline earth metal hydride.

9. Apparatus according to Claim 8, in which the solid electrolyte comprises lithium, sodium, barium or calcium hydride.

10. Apparatus according to any of Claims 6-9, in which the reference material consists of a metal/metal hydride mixture.

11. Apparatus according to Claim 10, in which the reference material consists of a calcium/calcium hydride mixture.

12. Apparatus according to any of Claims 6-11, in which the external surface of the solid electrolyte is sealed from the atmosphere by a layer of metal foil.

13. Apparatus according to any of Claims 6-12, in which an internal electrode passes through a seal in one end of the tubular probe to make electrical contact with the internal surface of the solid electrolyte at the other end of the tubular probe, and there is an external electrode adapted to contact the substance when the probe is in use.

14. Apparatus according to any of Claims 6-13, comprising a handle provided with insulation and incorporating electrically conducting members for connection to external and internal electrodes.

15. Apparatus according to any of Claims 6-14, substantially as hereinbefore described and illustrated with particular reference to the accompanying diagrams, Figures 1 and 2.

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Printed for Her Majesty's Stationery Office,
by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.

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3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

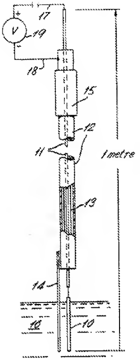

Fig. 2

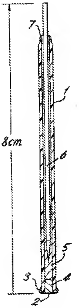

Fig 1

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Sheet 2

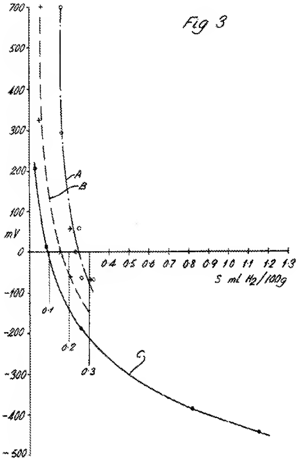

Fig 3

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Sheet 3

Fig. 4